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(71) Applicant: **Monsanto Company**
Patent Department 800 North Lindbergh Boulevard
St. Louis Missouri 63167(US)

(72) Inventor: **Chan, Albert Sun-Shi**
1522 Lynndale Drive
St. Charles Missouri 63301(US)

(74) Representative: **McLean, Peter et al,**
Monsanto Europe S.A. Patent Department Avenue de
Tervuren 270-272 Letter Box No 1
B-1150 Brussels(BE)

(54) Improved hydroformylation process to prepare glycol aldehydes.

(57) Formaldehyde is reacted with hydrogen and carbon monoxide with rhodium catalyst in the presence of phosphine ligands having electron-withdrawing substituents, obtaining high selectivity to glycol aldehyde with a stable catalyst system.

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IMPROVED HYDROFORMYLATION PROCESS
TO PREPARE GLYCOL ALDEHYDES

This invention relates to improvements in the production of glycol aldehyde by the reaction of formaldehyde, carbon monoxide and hydrogen in the presence of rhodium catalyst and certain
5 phosphines.

Background of the Invention

Glycol aldehyde is a valuable intermediate useful in the synthesis of other organic compounds, and can be converted, for example, to ethylene glycol by hydrogenation. Processes for
10 the production of glycol aldehyde by the reaction of formaldehyde with carbon monoxide and hydrogen in the presence of certain rhodium catalysts are described in European Patent 0 002 908, and also in U.S. Patent No. 4,200,765.

Summary of the Invention

The improved process of the present invention is carried out by reacting formaldehyde, carbon monoxide and hydrogen (under temperature and pressure conditions conducive to the formation of glycol aldehyde) in the presence of rhodium catalyst and a phosphine in which there is an electron-withdrawing substituent on an aryl ring of the phosphine. The presence of such phosphines contributes to better reaction rate and higher selectivity to glycol aldehyde, particularly when an excess of phosphine is employed to enhance catalyst stability. The electron-withdrawing substituent makes the phosphine less basic. The product produced in the present process contains very little glycol aldehyde condensation product, in contrast to the tendency of amine promoters to cause production of considerable condensation product. Suitably substituted triaryl phosphines are usefully employed, e.g. tris (4-trifluoromethylphenyl) phosphine.

Detailed Description of the Invention

The rhodium catalyts used herein are comprised of a rhodium component in association with ligands, as described in detail in U.S. Patent No, 4,052,461, and the aforementioned European Patent No. 0002908. Generally, the rhodium component

of such catalysts is considered to be present in the form of a coordination compound. Phosphines with electron-withdrawing substituents, as described herein, are generally a component of the active catalyst, whether provided to the reaction medium as part of a catalyst or catalyst precursor, or provided separately to the reaction medium. In addition to the rhodium component and phosphine, such coordination compound can include carbon monoxide (CO) ligands, hydride (H) ligands, halide or pseudo-halide components, or various other ligands. The term "coordination compound" as used herein means a compound or complex formed by a combination of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which may also be capable of independent existence. The rhodium may be complexed with from 3 to 6 or so ligands, and can be in a form usually considered as neutral or essentially non-valent in common catalyst systems, or in cationic form as described in the aforesaid U.S. Patent 4,052,461. The catalyst can be supplied to the reactants in active form or in the form of various catalyst precursors, and the catalyst also may undergo changes in the course of the reaction, or from the effect of the reaction conditions.

The substituted phosphines utilized in the present invention are characterized by having an electron withdrawing group substituted on an aryl ring of a phosphine. The electron-withdrawing

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group will ordinarily be in a position so as to have a strong effect upon a carbon-to-phosphorus bond of the phosphine, preferably in para-position of an aryl ring attached to phosphorus. One or
5 more of the electron-withdrawing substituents can be present in an aryl ring, but one effective group is sufficient so that there is ordinarily no need for more than one such group. The aryl rings can also contain other substituents, although
10 strongly electron-donating groups should ordinarily be avoided. Triaryl phosphines with an electron-withdrawing group in para-position to the phosphorus are preferred. However, phosphines with substitution of electron-withdrawing groups
15 in an aryl ring in ortho or meta positions can be employed, provided the substitution is effective to lower the basicity of the phosphine, making it less basic than triphenyl phosphine.

A number of electron-withdrawing groups are
20 known to the art, e.g. trifluoromethyl, nitro, and cyano groups, and in general electron-withdrawing groups characterized by suitable Hammett values can be used. The substituents on the phosphorus of the phosphines can be the same or different,
25 although it is generally more convenient for the groups to be the same. It is preferred that the aryl groups on which the electron-withdrawing groups are substituted be phenyl groups. Examples of phosphines with electron-withdrawing group
30 substitution include tris(4-trifluoromethylphenyl)phosphine, tris(4-cyanophenyl) phosphine, tris(4-nitrophenyl) phosphine, tris(3-methyl-4-trifluoromethylphenyl) phosphine, tris(2-fluoro-4-trifluoromethyl-6-fluoro-

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methylphenyl)phosphine, phenylbis-(trifluoromethylphenyl) phosphine, 4-cyanophenyl-bis(4-trifluoromethylphenyl) phosphine, etc. Aryl groups with acyl, e.g. 5 -COOC₂H₅, groups can be used, although the carboxyalkyl or other ester groups may tend to be hydrolyzed and could interfere to some extent in the desired reaction. Aside from the required electron-withdrawing substituents on the aryl 10 groups, it is convenient for the aryl groups on the phosphorus to be completely hydrocarbon, but other substituents can be present, particularly, non-interfering and relatively inert substituents such as fluorine atoms, for example. 15 Phosphines with three substituted phenyl groups, P(C₆H₄X)₃, where X is an electron-withdrawing group, are convenient for use, and those with X in the para position are preferred.

20 In the present invention, it is desirable to employ strongly electron-withdrawing groups, such as those having σ_p^0 values of at least 0.4, with the σ_p^0 value being that from the Hammett equation.

The Hammett equation is:

$$\log \frac{k}{k_0} = \sigma p$$

25 and for XC₆H₄ -

k_0 is the rate constant for X=H

k is the constant for the group X

p is the constant for a given reaction

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under given conditions
 σ is a constant characteristic of X

Hammett σ values are available for various group substituted at the p or m positions of phenyl rings. A positive value of σ indicates an electron withdrawing group, and such groups help reactions in which σ is positive. The σ^o_ρ value contemplates reactions at a site effectively insulated from \uparrow electrons of the benzene rings. The Hammett equation and sigma values are discussed in "Advanced Organic Chemistry", Jerry March, 2nd Ed., McGraw-Hill, New York, N.Y, (1977), at pages 251-259, and σ^o_ρ values are given in a table on page 256 which includes:

Group	σ^o_ρ
CF ₃	0.54
CN	0.66
NO ₂	0.83
CH ₃ CO	0.47

While the trifluoromethyl group is not as strongly electron-withdrawing as some other groups, aryl phosphines containing trifluoromethyl substituents can be conveniently prepared by a Grignard reaction, and the trifluoromethyl group is stable under reaction conditions. The cyano group is also relatively stable, but the nitro, group while effective, may tend to be used up under reaction conditions by reaction with carbon monoxide.

It is preferred that the electron-withdrawing group be in the para position of the aryl ring.

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However, such substituents in the meta or ortho positions still have some effect and are suitable for use as strongly electron-withdrawing groups in the present invention if the effect on basicity or
5 related properties of phosphines with such substituents is equal to or greater than that of a para-substituted electron-withdrawing group with a σ_p value of 0.4 or greater.

The substituted phosphines employed herein
10 are either coordinated to the rhodium atom to form the coordination compound or complex, or present as the free compound, i.e. uncoordinated or uncomplexed, or in both forms, in the reaction solution containing the rhodium coordination
15 complex. In the free compound state such compound has the potential to become coordinated to the rhodium atom via a ligand exchange reaction with a different ligand already coordinated to the rhodium atom.

20 Suitable organo phosphorus ligands which may comprise part of the ionic or neutral rhodium coordination compound used in this invention are those containing trivalent phosphorus and are referred to in this specification as phosphines.
25 Phosphines are useful ligands in the present catalysts, and phosphines, without electron-withdrawing substituents as described herein, can be usefully employed as catalyst ligands herein without significant adverse effects
30 in reaction rates if the amount of such phosphines is relatively low, such as not over 2 or 3 mols of such phosphine per rhodium atom. Thus, if desired, the catalyst can be provided to the

reaction medium with ordinary triphenyl phosphine as a ligand, and then the excess phosphine for catalyst stabilizing purposes can be that with electron-withdrawing substituents as described herein. Also, the small amount of phosphine coordinated with the rhodium can have substituents other than aryl groups on the phosphine, e.g. alkyl groups, but for the phosphine used in excess to have relatively less basic properties, it is appropriate to have only aryl groups on the phosphorus and to have electron-withdrawing substitution as described herein.

For phosphine ligands of the catalyst itself, organic radicals of any size and composition may be bonded to the phosphorous, and the radicals are preferably selected from the group consisting of aryl and alkyl groups. The more preferred ligands are those consisting of at least one but preferably two or three aryl groups as the organic moieties. For example, preferred modifying ligands are illustrated by the following structural formulae PR_3 where R is e.g. phenyl (C_6H_5-), or tolyl ($CH_3C_6H_4-$), xylyl ($CH_3C_6H_3CH_3$), e.g. $P(C_6H_5)_3$, $P(CH_3C_6H_4)_3$.

The phosphine ligands, and, if desired, other ligands, satisfy the coordination number of the central rhodium atom, and thus form a rhodium-containing complex. The term coordination compound or coordination complex means a compound or complex formed by combination of one or more electronically rich molecules or atoms, e.g., triphenylphosphine, carbon monoxide, 1,5-cyclooctadiene, (herein referred to as COD),

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with one or more electronically poor molecules or atoms, e.g. rhodium.

The rhodium complexes used in the present invention are ionic or neutral compounds, with the ionic ones having a non-complexing anionic moiety and the neutral ones containing halide, pseudo halide or hydride moiety. These have the general formula RhL_xAn . In this formula, in the case of the ionic ones, rhodium moiety is RhL_x^+ and the non-coordinating anionic moiety AN^- is exemplified by BF_4^- , ClO_4^- , PF_6^- , NO_3^- , and SiF_6^{2-} , and in the neutral ones An is halide, pseudo halide or hydride.

In the above formulae L is a ligand, (either the same or different ligands as described herein) and x varies from 2 to 5. The ligand L may or may not be a phosphine. For example, in the case where $[Rh(Ph_3P)_3]^+$ is employed as the rhodium-containing cation, Ph_3P is the ligand L. In the case where $[Rh(COD)(Ph_3P)_2]$ is employed as the rhodium-containing cation, Ph_3P and COD are the ligands L. In the case where $[Rh(COD)_2]^+$ is employed as the rhodium-containing cation, COD is the ligand L, and an excess of tris(trifluorophenyl)phosphine or similar phosphine is furnished to the reaction solution. In cases where the ligand L is not a phosphine, it may be a ligand displaceable by carbon monoxide under reaction conditions, e.g. COD. Examples of the ligand L include:

mono-enes of 2 to 12 carbon atoms.
dienes of 4 to 12 carbon atoms,

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trienes of 6 to 16 carbon atoms,
alkynes of 2 to 12 carbon atoms,
ketones of 3 to 12 carbon atoms,
nitriles of 2 to 12 carbon atoms,
5 N-alkylamines of 2 to 12 carbon atoms,
N-N-dialkylamides of 3 to 12 carbon atoms,
sulfoxides of 1 to 12 carbon atoms,
tertiary organo phosphorus compounds of
3 to 90 carbon atoms,
10 tertiary organo arsenic compounds of
3 to 90 carbon atoms,
tertiary organo antimony compounds of
3 to 90 carbon atoms,
carbon monoxide and combinations thereof.

15 The ionic or neutral rhodium compounds
described above are utilized in the present
invention as a means of introducing rhodium into
the reaction solution and are sometimes referred
to as catalyst precursors. Other forms of rhodium
20 may be used to form the rhodium catalyst, for
example, rhodium metal or rhodium metal on carbon
or rhodium halide may be introduced into the
system to form the rhodium catalyst.

In general, the relatively less basic
25 phosphines employed in the present invention can
be used with any of the usual rhodium catalysts or
catalyst precursors and their usual ligands.
However, while the ordinary phosphines can be used
as catalyst components in the present invention,
30 they are not employed in excess to stabilize the
catalyst, but any excess phosphines should be the
relatively less basic phosphines as described
herein. When phosphines, such as triphenyl

phosphine, are employed as catalyst ligands in amounts up to about 2 mols per rhodium atom, the reactivity and selectivity to glycol aldehyde is fairly good, but catalyst stability tends to be poor. In the present invention relatively high excesses of the less basic phosphines can be present and good reaction rates and selectivity to glycol aldehyde are still obtained. In the present invention it will generally be desirable to employ more than 3 mols phosphine per rhodium atom, and may be advantageous to have 5 or more mols phosphine per rhodium atom; and it is feasible to use much larger amounts of phosphine, such as 10 or 20 mols phosphine per atom of rhodium, on up to 50 or more mols.

The present reaction can conveniently be effected in a solvent which favors the production of glycol aldehyde over that of methanol, which generally requires a polar solvent. Some amides have been found to be particularly useful as solvents in the present process and to favor production of glycol aldehyde over that of methanol, the amides being characterized by the absence of free hydrogen on the amido nitrogen atom. N,N-disubstituted amides, i.e. amides with two organo substituents, are useful, the amides

being compounds characterized by
$$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NRR}' \end{array}$$
 where R and R' are organo groups, and may usually be hydrocarbyl groups. The substituents on the nitrogen are often alkyl groups, particularly lower alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, isopentyl, hexyl, etc. The amides are generally the amides of lower carboxylic

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acids, such as formic, acetic, propionic, hexanoic, etc. There is some variation in selectivity to glycol aldehyde with the variation in the chain length of the acid amide and the substituents on the nitrogen. The acetamides give particularly good results, but there is some loss in selectivity with increasing chain length of the nitrogen substituents on these and other amides. However another factor to be considered is suitability of the solvent for subsequent product separation procedures. Aqueous extractions may be employed, and a water immiscible reaction solvent is appropriate for such extraction procedure. The simple amides like dimethylformamide are water soluble but the amides tend toward water immiscibility with increasing chain length, particularly of hydrocarbon moieties, as with alkyl substituents on the nitrogen atom, and immiscibility is reached with sufficiently long chains. Thus di-n-butylformamide and di-isopentylformamide are suitable solvents for aqueous extraction procedures and are also suitable for conducting the hydroformylation reaction. In general, aprotic organic amides are useful solvents for the process of the present invention.

If desired, amines and such solvents can be used in the present invention with acceptable reaction rates. However, amines tend to cause condensation of the glycol aldehyde

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product, and their use is unnecessary in the present invention in which good rates and catalyst stability are obtainable in amide solvents in the presence of certain substituted phosphines as
5 described herein.

The hydroformylation processes of this invention are generally carried out at somewhat elevated pressures and temperatures, but in most instances relatively mild temperatures and
10 pressures are not only desirable, but preferable. Generally higher pressures provide the best reaction rates and selectivity but very mild pressures may be used if optimum reaction rates and selectivity are not required. For example,
15 pressures from 3447.38 kPa up to 41,368.54 kPa or higher can be used. Pressures in the range of 6894.76 kPa to about 20,684.27 kPa are generally convenient. The processes are temperature dependent and it is generally desirable to use moderate temperatures
20 of the order of 70°C. up to 150°C., and preferably from 90°C. up to 120°C.

The pressures referred to above are usually attained by the quantities of carbon monoxide and hydrogen charged to the reaction zone or system,
25 which is normally provided by an autoclave or other pressure resistant vessel. While the CO and H₂ react in a 1:1 mole ratio in the hydroformylation process, it is not necessary to have them present in such ratio for the reaction.
30 The CO and H₂ may conveniently be used in a mole ratio of about 1:1 as available in synthesis gas,



but can also be employed in widely varying ranges, such as CO:H_2 mole ratios varying from about 10:90 to 90:10. Usually, however, it is desirable to employ CO:H_2 mole ratios in the range of about 4:1 to about 1:2, and to avoid large excesses of hydrogen thereby suppressing methanol production.

The formaldehyde employed in the processes can be utilized in any form which will generate formaldehyde under the reaction conditions. A preferred form of formaldehyde is paraformaldehyde.

The amount of catalyst employed in the hydroformylation processes herein does not appear to be critical and can vary considerably without adversely affecting the course of the reaction. In any event, the amount of catalyst used should be sufficient to catalyze the hydroformylation of formaldehyde with carbon monoxide and hydrogen to form glycol aldehyde, and, preferably, should be sufficient to achieve a reasonably practical reaction rate. Generally, the rhodium catalysts are used in amounts sufficient to provide at least about 0.001 gram atoms of rhodium, and up to about 0.09 gram atoms of rhodium, per liter of the reaction medium. The preferred amounts for most purposes are in the range of from about 0.003 to about 0.03 gram atoms per liter. The concentration of formaldehyde can vary widely, for example, from less than 0.1 mole per liter of reaction medium to over 3 moles per liter of reaction medium; concentrations in the range of about 1 mole to about 2 moles per liter may be convenient for use.



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The present invention has the advantage of providing a process with good reaction rate and high selectivity to glycol aldehyde, which is conducted under conditions contributing to good catalyst stability. Rhodium catalysts in systems with little or no excess phosphine ligand give fairly good reaction rates, but tend to be unstable and lose activity. The presence of additional amounts of the usual phosphines improves the catalyst stability, but tends to lower the reaction rate and selectivity to glycol aldehyde. However, when the phosphine added in excess is a properly substituted phosphine as described herein, the desired catalyst stability is obtained, with retention of good reaction rate and selectivity to glycol aldehyde. Thus an excess of phosphine with electron-withdrawing aryl substitution can be employed and reaction rates can be obtained approaching or equal to those obtainable with a rhodium catalyst employing a triphenylphosphine to rhodium ratio of 2 or 3 to 1. Formaldehyde conversions of 75 to 80% or so can be obtained with reasonably short batch reaction times, along with conversions to glycol aldehyde of 85 to 90% or more. Correspondingly, condensation of the glycol aldehyde to other products is kept relatively low. The advantages of the use of properly substituted phosphines, as described herein, is particularly evident when a fairly high excess of phosphine is employed, as 5 or more moles of phosphine per rhodium atom.

The following specific examples are intended to illustrate the processes of this invention, but not to limit the scope thereof. In

these examples the term "m mole" is intended to mean milli moles.

Example 1

A 300 ml stainless steel autoclave equipped with a Magnedrive stirrer was charged with 0.0973g
5 of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, (0.5 mmol Rh), 2.32 g tris-4-(trifluoromethylphenyl)phosphine, (5 mmol), 6.2g paraformaldehyde (contains 97% formaldehyde, 0.2 mole) and 100 ml N,N-Dimethylacetamide (solvent). The reactor was then heated to 110°C under 12,410.56
10 kPa $\text{CO}:\text{H}_2$ (1:1). The reaction was run at 110°C under 17,236.89 kPa total pressure for 1.5 hours. Analyses of the products indicated 79% conversion of formaldehyde. The selectivities were: 91% for glycolaldehyde; 2% for methanol; about 1% glyoxal;
15 trace amount of glycerol; and about 6% C_3 and C_4 aldehydes and ketones (condensation products).

Upon substituting tris-(4-cyanophenyl) phosphine for the phosphine in the procedure of Example 1, and carrying out the procedure as
20 described in Example 1, similar results, including high selectivity to glycolaldehyde, are to be expected.

Example 2

The conditions were the same as Example 1
25 except that the amount of tris(4-trifluoromethylphenyl)phosphine was doubled. Analyses of the products after 2 hours of reaction indicated

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77% conversion of formaldehyde. The selectivities were: 90% for glycolaldehyde; 2.6% methanol; 5% for C₃ and C₄ aldehydes and ketones. Small amounts of glyoxal and glycerol were also observed.

5

Example 3

The conditions were the same as Example 1 except that the Rh complex charged was 0.345g RhCl(CO)(PPh₃)₂, (0.5 mmol). Product analysis after 2 hours of reaction indicated 75% conversion of formaldehyde. The product selectivities were: 93% for glycolaldehyde; 3% for methanol; about 4% for C₃ and C₄ aldehydes and ketones.

10

Example 4

(Comparison Example)

15

The conditions were the same as Example 1 except that the Rh complex charged was 0.345g RhCl(CO)(PPh₃)₂, (0.5 mmol), and the phosphine was 3.7g triphenylphosphine, (14 mmol). Product analysis after 2 hours of reaction indicated less than 44% conversion of formaldehyde. The selectivities for glycolaldehyde and methanol were 43% and 11%, respectively. the rest of the products were higher boiling byproducts.

20

Example 5

25

(Comparison Example)

The conditions were the same as in Example 4 except that the added triphenylphosphine was 0.393g. Product analysis after 2 hours of reaction indicated 65% conversion of formaldehyde.

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The selectivities for glycolaldehyde and methanol were 82% and 6%, respectively.

- 5 The tris(4-trifluoromethylphenyl) phosphine used in the above examples was prepared by reaction of p-bromobenzotrifluoride with magnesium to form a Grignard reagent, which was reacted with phosphorus trichloride; see G.R. Miller, A.W. Yankowsky, and S. O. Grim, J. Chem Physics, Vol. 51, 3185 (1969).

WHAT WE CLAIM IS:

1. The process of preparing glycol aldehyde which comprises reacting formaldehyde, carbon monoxide and hydrogen in the presence of rhodium catalyst and a triarylphosphine which has an electron-withdrawing substituent on an aryl ring.
2. The process of Claim 1 in which reaction is conducted at temperatures of about 70° to about 150°C . and pressures of about 3,447.38 pKa to about 41,368.54 kPa.
3. The process of Claim 1 in which phosphine is present in excess of 3 mols per atom of rhodium.
4. The process of Claim 1 in which phosphine having an electron-withdrawing substituent on an aryl ring is present in an amount of at least about 5 mols per atom of rhodium.
5. A process for the production of glycol aldehyde which comprises reacting carbon monoxide, hydrogen and formaldehyde in a solvent system at elevated temperature and pressure in the presence of a rhodium catalyst effective to produce glycol aldehyde from such reactants, and having present a triaryl phosphine less basic than triphenylphosphine and in which there is a strongly

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electron-withdrawing group substituted on an aryl ring of the phosphine.

6. The process of Claim 5 in which an organic amide solvent is employed.

5 7. The process of Claim 6 in which the amide is an N,N-dialkylamide of a lower carboxylic acid.

10 8. The process of Claim 5 in which the triarylphosphine is tris(4-trifluoromethylphenyl) phosphine.

15 9. The process of Claim 5 in which triaryl phosphine is present which is less basic than triphenyl phosphine and has an electron-withdrawing aryl substituent having a σ_p^0 value of at least 0.4.

10. The process of Claim 5 in which an electron-withdrawing substituent is in para position.

20 11. The process of Claim 5 in which an electron-withdrawing group is selected from trifluoromethyl, cyano, and nitro groups.

25 12. The process of Claim 5 in which phosphine present is represented by $P(C_6H_4X)_3$ in which X is an electron withdrawing group with a σ_p^0 value of at least 0.4.

13. The process of Claim 12 in which X is trifluoromethyl.

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14. The process of Claim 5 in which carbon
monoxide to hydrogen ratios are in the range of
about 4:1 to about 1:2, temperatures are in the
range of about 90° to about 120°C. and pressures
5 are in the range of about 6,894.76 to about 20,684.27
kPa.

15. The process of Claim 14 in which a
substituted triphenyl phosphine is present in
which each phenyl group has an electron-
10 withdrawing substituent in para-position to
phosphorous, such substituent having a σ_p^0 value
of at least 0.4.

16. The process of Claim 15 which
reaction is carried out in aprotic organic amide
15 solvent employing the substituted triphenyl
phosphine in amount in excess of 3 moles per atom
of rhodium.

17. The process of Claim 16 in which
rhodium catalyst is present in an amount in the
20 range of about 0.001 gram atom to about 0.09 gram
atom per liter of reaction medium.

18. The process of Claim 17 in which tris
(4-trifluoromethylphenyl) phosphine is the
substituted triphenylphosphine.